

## PATENT ABSTRACTS OF JAPAN

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## (54) POSITIVE TYPE PHOTO-RESIST COMPOSITION

## (57)Abstract:

PURPOSE: To provide a positive type photo-resist composition having high sensitivity and excellent preservation stability and preventing the occurrence of foreign matter with the passage of time when it is used as a solution by adding an acid compound to a 1,2-naphthoquinone azide photosensitive agent and an alkali-soluble resin.

CONSTITUTION: An acid compound is added to a positive type photo-resist composition containing an alkali-soluble resin and a 1,2-naphthoquinone azide photosensitive agent. This acid compound is an organic acid such as p- toluenesulfonic acid, acetic acid, oxalic acid, or phosphoric acid or an inorganic acid such as hydrochloric acid, nitric acid, or sulfuric acid. The content of the acid compound is set to 0.05-1wt.% against the photo-resist composition. The resist is soluble in alkali when exposed, however the photosensitive agent is deposited as foreign matter in an alkaline solution when it is not exposed, thus the solution is made to be on slightly acid side to neutral so that foreign matter is hardly deposited.

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CLAIMS

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[Claim(s)]

[Claim 1] A positive type photoresist constituent characterized by containing an acid compound in alkali fusibility resin and a positive type photoresist constituent containing 1 and 2-naphthoquinonediazide system sensitization agent.

[Claim 2] A positive type photoresist constituent according to claim 1 with which said acid compound is characterized by being p-toluenesulfonic acid, an acetic acid, oxalic acid, a phosphoric acid, a hydrochloric acid, a nitric acid, or a sulfuric acid.

[Claim 3] Claim 1, a positive type photoresist constituent of two publications with which a content of said acid compound is characterized by being 0.05 - 1 % of the weight to a photoresist constituent.

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the positive type photoresist constituent which was excellent in conservation stability without generating of the foreign matter accompanying time amount progress, when using as high sensitivity and a solution about a positive type photoresist in the so-called manufacturing process of a semiconductor, the manufacturing process of the liquid crystal display containing TFT, and manufacturing processes, such as various etching parts.

[0002]

[Description of the Prior Art] With the improvement in whenever [ integration ], detailed-ization progresses, and it becomes the time of a VLSI, and has become the time of layout of submicron order. In connection with it, the demand to photolithography technology is also severe every year. In the technology of this photolithography, the negative-mold photoresist which added the bis-azide system cross linking agent to cyclized rubber as a resist conventionally has been used. However, since this type was solvent development, it has the problem of swelling and was not able to obtain resolution of 3.0 micrometers or more. Furthermore, the time of a half micron has come from submicron one, and they are starting [ put ] and the contact dew of actual size to a turning point in material. However, when a stepper was used, the long duration important point was carried out to exposure, and there was a problem that a throughput fell.

[0003] The proposal of using for a sensitization agent recently what esterified the 1 and 2-naphthoquinonediazide-5-sulfonic-acid or 1, and 2-naphthoquinonediazide-4-sulfonic acid to the hydroxyl group of a 2, 3, 4, and 4'-tetra-hydroxy benzophenone for the improvement in sensitivity is made (JP,62-28457,B). However, what esterified the 1 of 2, 3, 4, and 4'-tetra-hydroxy benzophenone and 2-naphthoquinonediazide-5-sulfonic-acid or 1, and 2-naphthoquinonediazide-4-sulfonic acid was lacking in the solubility to a solvent, when it was made to dissolve to some extent, it becomes easy to generate a foreign matter in a solution, and the thing of high sensitivity was seldom obtained. Therefore, the proposal of using for four hydroxyl groups of a 2, 3, 4, and 4'-tetra-hydroxy benzophenone what does not esterify completely a 1 and 2-naphthoquinonediazide-5-sulfonic-acid or 1, and 2-naphthoquinonediazide-4-sulfonic acid 100% a sake [ on a dissolution disposition ] is also made (JP,61-185741,A).

[0004] However, when the defect in which the conventional positive type photoresist constituent which described above what is not esterified completely 100% has four hydroxyl groups of a these 2, 3 and 4, and 4'-tetra-hydroxy benzophenone cannot fully be conquered and it used as high sensitivity and a solution, the present condition was that the constituent without generating of the foreign matter accompanying the passage of time is not found out.

[0005]

[Problem(s) to be Solved by the Invention] In the manufacturing process of a semiconductor, the manufacturing process of the liquid crystal display containing TFT, and manufacturing processes, such as various etching parts, especially the place that it is made in order that this invention may solve such a trouble, and is made into the technical problem is to offer the positive type photoresist constituent which was excellent in conservation stability without generating of the foreign matter accompanying the passage of time, when using as high sensitivity and a solution.

[0006]

[Means for Solving the Problem] In order that this invention may solve this technical problem, in alkali fusibility resin and a positive type photoresist constituent containing 1 and 2-naphthoquinonediazide system sensitization agent, a positive type photoresist constituent characterized by making an acid compound contain is offered, and it is characterized by said acid compounds being inorganic acids, such as organic acids, such as p-toluenesulfonic acid, an acetic acid, oxalic acid, and a phosphoric acid, a hydrochloric acid, a nitric acid, and a sulfuric acid. Moreover, a content of said acid compound offers a positive type photoresist constituent characterized by being 0.05 - 1 % of the weight to a photoresist constituent.

[0007] This invention can obtain a positive type photoresist constituent which was excellent in conservation stability which does not have generating of a foreign matter accompanying the passage of time simply, when using as high sensitivity and a solution, without reducing many properties of the conventional positive type photoresist by making 1 and 2-naphthoquinonediazide system sensitization agent and alkali fusibility resin add said acid compound.

[0008] As a content of an acid compound concerning this invention, what was contained 0.075 to 0.15% of the weight preferably is used 0.05 to 1% of the weight to a photoresist constituent. Many properties of a resist fall that a content is more than this, and an effect does not show up that a content is less than [ this ].

[0009] As alkali fusibility resin, novolak resin manufactured from a phenol or cresol, and formaldehyde, polyvinyl alcohol, polyvinyl alkylether, etc. can be mentioned.

[0010] As a 1 and 2-naphthoquinonediazide system sensitization agent 2, 3, 1 of 4-trihydroxy benzophenone, ester of a 2-naphthoquinonediazide-4-sulfonic acid, 2, 3, 1 of 4-trihydroxy benzophenone, ester of a 2-naphthoquinonediazide-5-sulfonic acid, 1 of a 2, 3, 4, and 4'-tetrahydroxy benzophenone, ester of a 2-naphthoquinonediazide-4-sulfonic acid, 1 of a 2, 3, 4, and 4'-tetrahydroxy benzophenone, ester of a 2-naphthoquinonediazide-5-sulfonic acid, 2, 2', 3 and 4, 1 of a 4'-pentahydroxy benzophenone, ester of a 2-naphthoquinonediazide-4-sulfonic acid, 2, 2', 3 and 4, 1 of a 4'-pentahydroxy benzophenone, ester of a 2-naphthoquinonediazide-5-sulfonic acid, etc. can be mentioned.

[0011] As an example of a solvent, ester, such as cellosolve system solvents, such as ketones, such as an acetone, a methyl ethyl ketone, a cyclohexanone, and an isoamyl ketone, methyl cellosolve, ethylcellosolve, butyl cellosolve, methyl-cellosolve acetate, and ethylcellosolve acetate, methyl acetate, ethyl acetate, and butyl acetate, can be mentioned. These may be used independently, and two or more kinds may be mixed and they may be used.

[0012] About operation of an acid compound of this invention, it melts to a suitable solvent which described above a positive type photoresist constituent of this invention on a substrate first, prebakes by applying this with a spinner etc., and exposes through a mask pattern using an ultrahigh pressure mercury lamp etc. Next, an image faithful to a mask pattern can be obtained by this being immersed in an alkaline aqueous solution.

[0013]

[Function] The positive type photoresist which is neutrality in the state of a resist consists of alkali fusibility resin and an alkali insolubility sensitization agent. If a resist is exposed, it will become meltable to alkali, but if the inside of a solution becomes being unexposed on an alkali

side, the sensitization agent which is a foreign matter deposits. Therefore, it changes into the condition that a foreign matter cannot deposit easily due to making it an acid side a little than neutrality. Therefore, the positive type photoresist constituent of this invention has very good conservation stability. Therefore, if these constituents are used as a solution, most generating of the foreign matter accompanying the passage of time will not be seen. Moreover, shelf life can be stabilized by adding an acid compound, without sensitivity falling compared with what used the sensitization object of a publication for these people's Japanese-Patent-Application-No. No. 291852 [ five to ] specification.

[0014]

[Example]

<Example 1> It was made to dissolve in methyl-cellosolve acetate 39g completely, and 1 of a 2, 3, 4, and 4'-tetra-hydroxy benzophenone and 4.84g of esterification objects of a 2-naphthoquinonediazide-5-sulfonic acid were used as the solution 1. Moreover, 17.16g (weight average molecular weight 25000, polystyrene conversion) of cresol novolak resin was dissolved in methyl-cellosolve acetate 39g, and it considered as the solution 2. A solution 2 and 0.1g of p-toluenesulfonic acid were completely dissolved in the solution 1 by 65-75 degrees C and 15min, this solution was filtered with the 0.2-micrometer filter, and the photoresist was prepared.

[0015] The spin coat of this photoresist was carried out so that thickness might become 8500A to a chromium substrate, and it prebaked in 90 degrees C and 50 minutes. an ultrahigh pressure mercury lamp aligner (product made from Canon : "PLA-500FA") -- using -- 1.8 mJ/cm<sup>2</sup> - 42.8 mJ/cm<sup>2</sup> up to -- light exposure was shaken and exposed. Then, with the solution dissolved in the water 1000 weight section, the sodium-hydroxide 4 weight section and the sodium-carbonate 5 weight section were developed for 40 seconds, and were washed in cold water well.

[0016] Next, postbake was carried out and sensitivity and the remaining rate of membrane of the unexposed section were measured. A result is shown in a table 1. Moreover, the result of the conservation stability in the temperature of 20 degrees C was shown in a table 2.

[0017] <Example 1 of a comparison> It was made to dissolve in methyl-cellosolve acetate 39g completely, and 1 of a 2, 3, 4, and 4'-tetra-hydroxy benzophenone and 4.84g of esterification objects of a 2-naphthoquinonediazide-5-sulfonic acid were used as the solution 1. Moreover, 17.16g (weight average molecular weight 25000, polystyrene conversion) of cresol novolak resin was dissolved in methyl-cellosolve acetate 39g, and it considered as the solution 2. A solution 2 and 0.1g of 1% sodium-hydroxide solutions were completely dissolved in the solution 1 by 65-75 degrees C and 15min, this solution was filtered with the 0.2-micrometer filter, and the photoresist was prepared.

[0018] The resist pattern was obtained for this photoresist by the same method as an example 1. The result was shown in a table 1. Moreover, the conservation stability test in the temperature of 20 degrees C was performed also about this resist, and the result was shown in a table 2.

[0019] <Example 2 of a comparison> It was made to dissolve in methyl-cellosolve acetate 39g completely, and 1 of a 2, 3, 4, and 4'-tetra-hydroxy benzophenone and 4.84g of esterification objects of a 2-naphthoquinonediazide-5-sulfonic acid were used as the solution 1. Moreover, 17.16g (weight average molecular weight 25000, polystyrene conversion) of cresol novolak resin was dissolved in methyl-cellosolve acetate 39g, and it considered as the solution 2. A solution 2 and 0.1g of water were completely dissolved in the solution 1 by 65-75 degrees C and 15min, this solution was filtered with the 0.2-micrometer filter, and the photoresist was prepared.

[0020] The resist pattern was obtained for this photoresist by the same method as an example 1. The result was shown in a table 1. Moreover, the conservation stability test in the

temperature of 20 degrees C was performed also about this resist, and the result was shown in a table 2.

[0021] It was made to dissolve in methyl-cellosolve acetate 39g completely, and 4.84g of partial esterification objects of a 1 of 2, 3 and 4 which are averaged to <example 3 of comparison> sensitization agent and by which three hydroxyl groups are esterified, and 4'-tetra-hydroxy benzophenone, and 2-naphthoquinonediazide-5-sulfonic acid was used as the solution 1. Moreover, 17.16g (weight average molecular weight 25000, polystyrene conversion) of cresol novolak resin was dissolved in methyl-cellosolve acetate 39g, and it considered as the solution 2. The solution 2 was completely dissolved in the solution 1 by 65-75 degrees C and 15min, this solution was filtered with the 0.2-micrometer filter, and the photoresist was prepared.

[0022] The resist pattern was obtained for this photoresist by the same method as an example 1. The result was shown in a table 1. Moreover, the conservation stability test in the temperature of 20 degrees C was performed also about this resist, and the result was shown in a table 2.

[0023]

[A table 1]

	露度 (mJ/cm <sup>2</sup> )	残膜率 (%)
実施例1	17.1	96.3
比較例1	35.0	80.0
比較例2	22.4	95.0
比較例3	25.0	97.0

[0024]

[A table 2]

(単位 個/10μm)

保存日数	1日	2日	3日	5日	1週	2週	3週	4週	8週
実施例1	25	28	31	37	35	42	45	45	49
比較例1	125	365	476	645	783	934	1001	1276	1352
比較例2	153	302	435	523	794	807	1050	1428	2045
比較例3	27	34	37	40	48	42	40	45	50

\* 20℃保存品のパーティクル数変化: 経±0.5μm

[0025]

[Effect of the Invention] As shown above, the positive type photoresist constituent of this invention can suppress generating of a foreign matter easily by containing an acid little compound, without a resist property being inferior compared with the positive type photoresist of high sensitivity. In the example, even if one month or more passed, most generating of a foreign matter was not seen in the resist property and the photoresist constituent.

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